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FULLERENES IN ION-BASED CARBONACEOUS ALLOYS

INTRODUCTION

Theoretical idea of structure, phase transformation, iron and carbon interaction in iron-carbonaceous alloys are constantly developing and being revised with the appearance of new investigations results in this field. Thus, in connection with the detection of fullerene C_{60} in the structure of iron-based carbonaceous alloys, distinguishing with the amount and form of carbon (carbonyl iron, structural steel 10, 20, 45 before and after graphitization, chisel tool steel с У7, У8, У10, У12, gray pig iron СЧ15, СЧ18, СЧ25 and high-strength iron ВЧ45, ВЧ60) [1], there appeared fullerene trend within material science.

EXPERIMENTAL

The finding out mechanism and conditions of fullerene formations was carried out while studying the first stage of production of iron-carbonaceous alloys, namely blast furnace process. Some samples of blast furnace production raw material and products were prepared for investigation by spectral methods (mass- and infrared (IR) spectrometry):

1) of coal coke, being due to high contents of carbon (82,55%) a potential source of fullerenes;

2) of conversion pig iron ПЛ1 with different cooling conditions - in water with the starting temperature 20 ^{0}C (samples №1, №2) and in air (samples №3-№6).

3) of blast-furnace dust, contacting about 12% of carbon (taken from the system of dry dust precipitators, located in blas furnace.

The procedure of preparing is given in table 1.

Mass-spectral analysis was carried out with the apparatus MU-1201. Mass-spectra of positive ions of all tested samples showed the presence of fullerenes C_{60}, which is confirmed by their isotope compound. In mass-spectra of conversion pig iron there is some amount of fullerens $C_{60}F_{18}$ and $C_{60}F_{36}$. Similar result is shown by mass-spectra of negative ions.

Table 1 - The procedure of preparing samples

Sample	The procedure of preparing	Colour
Coke	Concentrated solution in carbon tetra chloride	Colourless
Blust furnace dust		
ПЛ1, Л4, Л5	1) cleaning the sample surface till metallic lustre; 2) separating chips; 3) dissolving in hydrofluoric acid; 4) extraction by carbon tetra chloride	

Some amount of fullerenes in tested samples was detected by IR spectrometry according to earlier developed procedure [2] (table 2). Analysis of IR spectra showed, that for conversion pig iron ПЛ1 there is little increasing fullerene amount with increasing cooling rate.

RESULTS

For comparison casting pig iron Л4, Л5 was taken while cooling in air and the dependence of fullerene amount on percentage contents of carbon for blast furnace pig iron was plotted (fig. 1). It's clear that with increasing percentage contents of carbon in pig iron fullerene amount decreases.

Table 2 - Results of blast furnace process samples IR spectra analysis

Sample	Amount of fulleren in 1 g of sample, 10^3 g	Amount of fulleren in 1 g of sample, 10^{-15}	Relative contents of fullerenes, %
Coke	24,375	20,22	0,0300
Pig iron ПЛ1 №1	3,762	3,121	0,0088
№2	3,624	3,007	0,0086
№3	3,321	2,755	0,0076
№4	3,384	2,807	0,0079
№5	3,542	2,938	0,0084
№6	3,229	2,679	0,0074
Л4	3,762	3,121	0,0092
Л5	3,636	3,016	0,0082

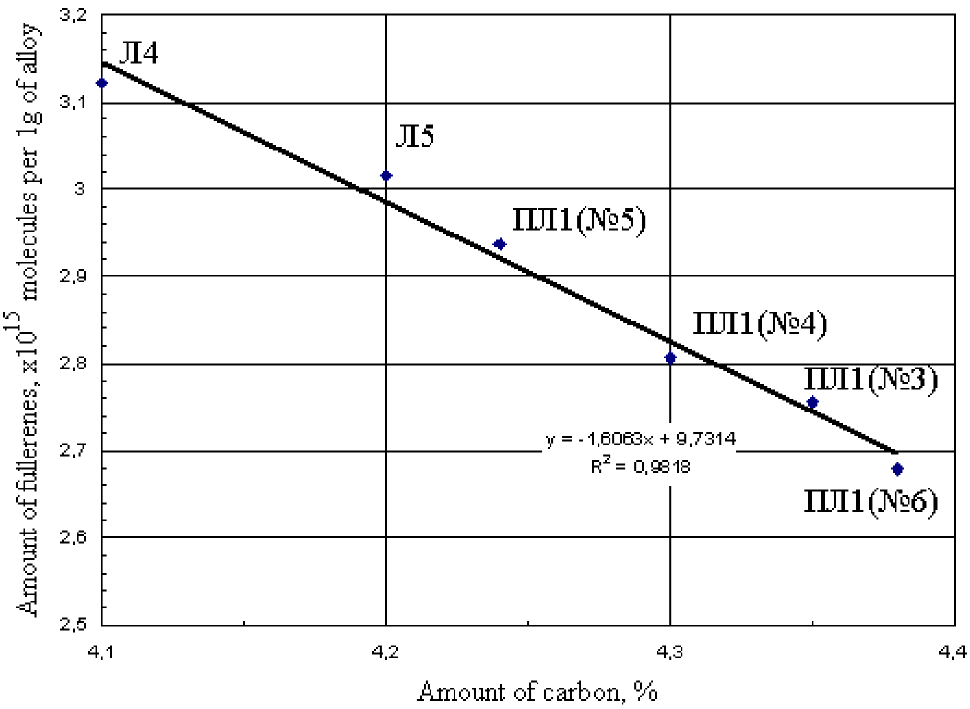
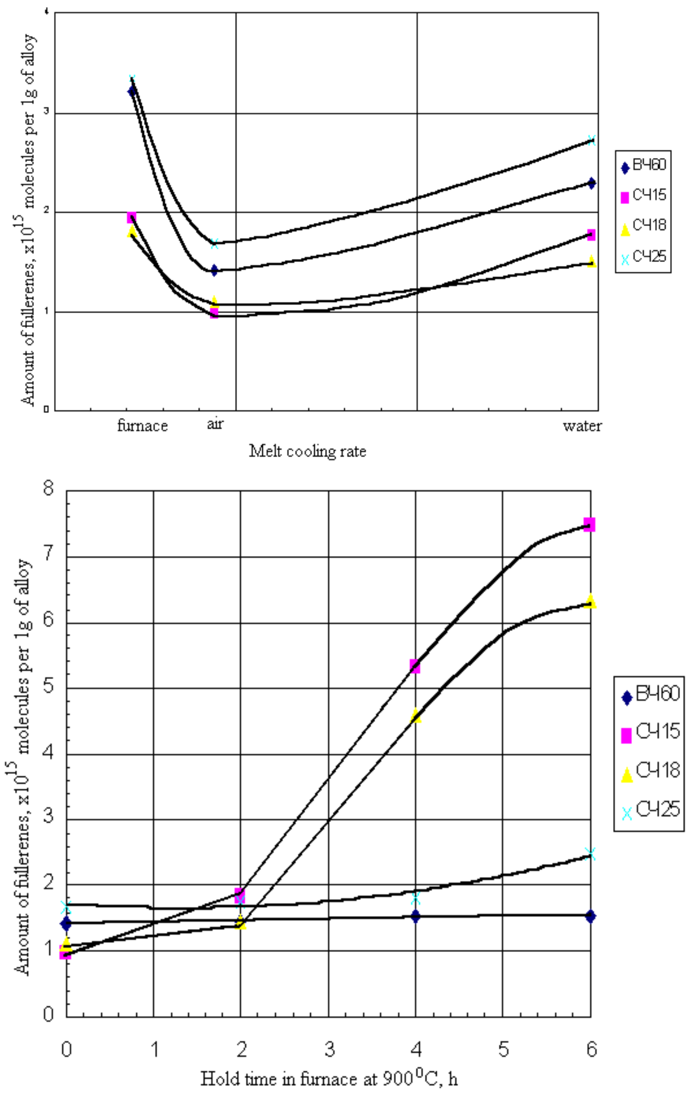


Fig.1 - Dependence of fullerenes amount on percentage contents of carbon for blast furnace pig iron

According to results of blast furnace process investigation an assumption, that some part of fullerenes transmit from coke to melt and then to alloy structure, and another part is forming during slow cooling of melt. So the dependence of melt cooling rate on fullerene amount was investigated samples of high-strength pig iron ВЧ60 and grey pig iron СЧ15, СЧ18 and СЧ25 were received by melting casting pig iron Л5. Different cooling rates were chosen: in air, in water, with a furnace, having starting temperature 900 ^{0}C, also samples were hold in a furnace for 2, 4, 6 hours at 900 ^{0}C with the following cooling in air [3].

In result of IR analysis of samples are given in fig. 2. It's evident that melt cooling rate in fact doesn't influence fullerene amount. Holding samples in a furnace at 900^{0}C shows the considerable increase of fullerene amount with increase of holding time for that pig iron, which has more free carbon, for example for СЧ15 fullerene amount was about seven times as large.

The increasing fullerene amount is as well observed while salurating metal with carbon atoms. For the first time this phenomenon was found out during investigating pyrolysis furnace worm pipe metal, in which carbon diffusion from coke, deposited on piper inner surface by hydrocarbon raw material processing, taken place [4]. In carburizing zone there were fullerenes C_{60} 5,5 times as large, than in base metal [5]. In this connection an assumption was made, that additional formation of fullerenes in carbonazed layer during chemico-thermal treatment (carburizing) is possible.



a

b

Fig. 2 - Dependence of fullerene amount on melt cooling rate (a) and on hold time in furnace at 900 ^{0}C (b)

For studying carburizing process some samples of carbonaceous steel of high quality

20 samples by remelting armco iron. The process of carburizing was carried out in carburizer "syntin", which is a multicomponent system, consisting of N_2-CO_2-CO-H_2-H_2O-CH_4. The process runs in electric mine furnace C105 at 925 ^{0}C. Samples were hold for 8,10 and 14 hours for receiving carbonized layer of different thickness and then were cooled in air.

For determining the depth of carbonized layer the microhardness distribution along the sample section was determined, in accordance with it chips were separated and samples were prepared for IR spectral analysis (see table 1). These results (fig. 3) allows to make the following conclusion: fullerene amount is four times as large in carbonized zone of samples after carburizing, than in base metal; increase of holding time in a furnace results in increase of fullerene amount in carbonized zone [6].

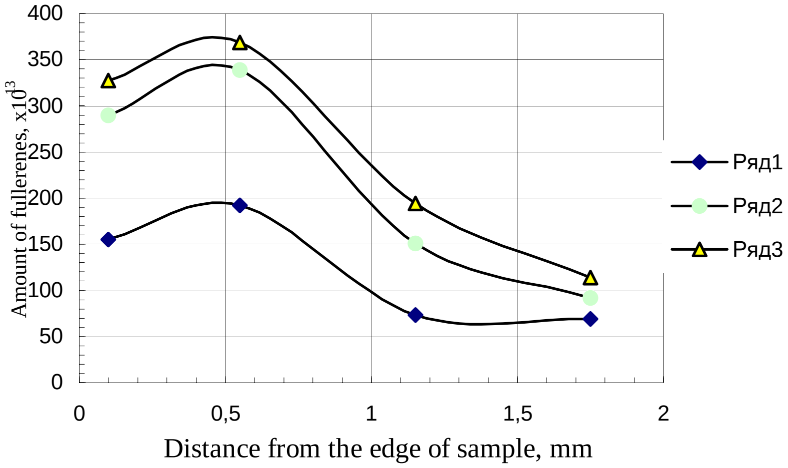


Fig.3 - Distribution of fullerene amount along sample depth, made of steel 20 after carburizing (row 1 - carburizing time 8 hours; row 2 - 10 hours, row 3 - 14 hours)

Termal treatment of samples - hardening at 860 ^{0}C and cooling in industrial spindle oil И20А with low tempering at 160 ^{0}C results in drasticincrease of fullerene amount on carbonized zone (fig. 4).

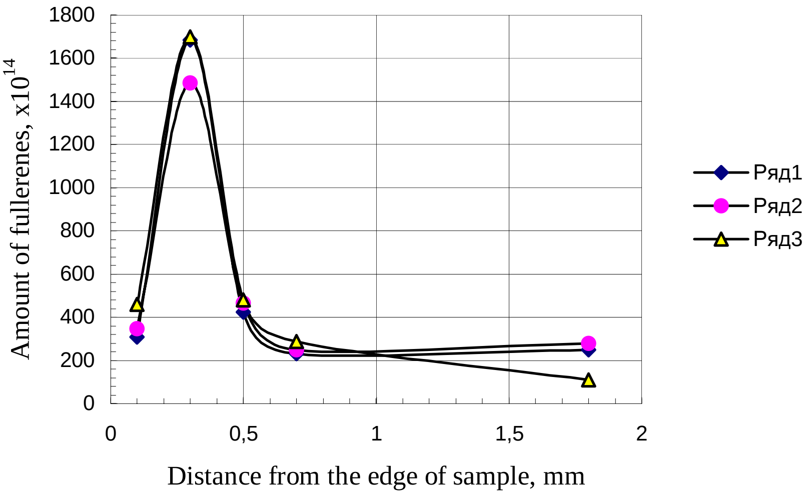


Fig. 4 - Distribution of fullerene amount along sample depth, made of steel 20 after carburizing and termal treatment (row 1 - carburizing time 8 hours; row 2 - 10 hours, row 3 - 14 hours)

Highly propononced extremum of fullerene content in carbonaceous layer at the depth

0,3 mm is attributed to the presence of barrier for intensive carbon diffusion into the depth of material due to porosity change.

In future it will help to create optimal technology of detail treatment for increasing wear-resistance and lifetime. For example, it is possible to separate surface layer 0,3 mm by means of mechanical treatment, exposing zone of maximal fullerene contents, displaying strong hardness - close to diamond hardness in condenced state.

CONCLUSIONS

1. For the first time there received the data of fullerene presence in coal coke and blast-furnace dust.

2. Two ways of fullerene formation in iron-carbon alloys have been experimentally substantiated. The first way is fullerene transition from coke. The second way is fullerene formation during structural and phase transition.

3. It has been shown that the amount of fullerenes in iron-based carbon alloys depends on a thermal treatment cycle: temperature, delay time, cooling rate.

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